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CROSSLINKED FINE PARTICLES AND CURABLE RESIN
COMPOSITION

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to a resin composition useful as an radiation curable resin composition; a thermosetting resin compositions or the like, and it relates to, in particular, a resin composition that can have all of a low viscosity, low shrink properties and a rapid-curability, unlike conventional curable resin compositions.

10 (2) Description of the Related Art

Radical-polymerization type radiation curable resin compositions are utilized in various surface fabrication fields because they are rapidly curable at low temperatures and give a cured coating film excellent in scuff resistance, chemical resistance and the like. The radiation curable resin compositions, however, usually tend to have a high viscosity at room temperatures. It is, therefore, necessary to reduce viscosity in order to facilitate their application.

20 Therefore, the uses of organic solvents or diluent monomers having a low viscosity are necessary for the viscosity reduction, resulting in problems taken up in recent years, such as reduction of the environmental impact by reduction of the volatile

organic compound (VOC) content, skin irritation caused by the diluent monomer, and a decrease in the curing rate of said resin composition.

In general, radiation curable resin-
5 compositions are remarkably shrunk in volume upon curing, and hence a method comprising adding a high-molecular weight oligomer or polymer has been adopted for reducing the percentage of shrinkage. However, when this method is adopted, the viscosity of said
10 resin composition tends to be increased to deteriorate the coating properties, and the curability tends to be deteriorated by the decrease of the reaction site concentration of the resin composition.

Also in the field of, for example, film
15 coating materials, radiation curable resin compositions draw attention. For instance, JP-A-3-252460 discloses a composition for coating material which comprises an ethylenic unsaturated compound having a molecular weight of 500 or less, a styrene-based polymer having
20 a softening point of 70°C or higher, and a photopolymerization initiator and is excellent in adhesive properties to various substrates, high gloss, blocking resistance, scratch resistance, water resistance, etc.

25 However, since the aforesaid composition contains the styrene-based polymer having no photo-reactivity, its viscosity tends to become so high that the coatability should be poor depending on the amount

of the styrene-based polymer added. Moreover, since a large amount of the photopolymerization initiator has to be incorporated into the composition in order to attain a high productivity, a large amount of the photopolymerization initiator remains in a cured coating film, resulting in a film product having the unpleasant odor of the photopolymerization initiator. Thus, no product having satisfactory overall performance characteristics could be obtained.

Also in the field of coating materials for wood coatings, radiation curable compositions of rapid curing type have come to be extensively used which entail a low energy cost and are good in productivity. Of the radiation curable compositions utilized in the said field, compositions containing an unsaturated polyester resin inter alia have been extensively used because they give a cured coating film excellent in finished appearance involving gloss, feeling of fleshiness, and are inexpensive.

However, in the case of a coating film of such a composition, the surface curing speed is lower than it in depth, resulting in an insufficient productivity of an applied and cured product. Moreover, since the internal strain of the cured coating film is increased by the cure shrinkage of one or more monomers and oligomers contained in the composition, the composition is disadvantageous in that the cured coating film tends to be cracked by the

repetition of heating and cooling.

For removing these defects, for example, JP-A-4-202213 discloses a composition using a maleic acid-based unsaturated polyester containing a specific
5 glycol component, and JP-A-5-202163 discloses a composition using an epoxy acrylate, a specific acryl polyol component and an isocyanate compound.

The composition disclosed in JP-A-4-202213, however, requires the use of styrene monomer as a
10 diluent for improving the coating efficiency. The use of styrene monomer deteriorates the surface curability and moreover, the work environment is harmed by odor diffused by the volatilization or the styrene monomer. The composition disclosed in JP-A-5-202163 also failed
15 to improve the work environment because it has a high viscosity and hence requires the use of a diluent such as an organic solvent, for improving the coating work efficiency to put the composition to practical use.

In recent years, printing inks curable by
20 active energy rays such as electron rays, ultraviolet rays, visible rays, etc. have been substituted for common oil inks in an increasing fields and used increasingly, because of their many advantages, such as speeding-up of printing, speedy delivery, hygienic
25 properties, etc. These printing inks comprise a composition containing a radical-polymerizable monomer, an oligomer and a coloring agent such as a pigment. As specific examples of the printing inks, the composition

systems co-using a diallyl phthalate-based polymer disclosed in, for example, JP-B-61-4861 and JP-A-3-212460 have been extensively used from the viewpoint of printability, curability, mar resistance, etc. These composition systems, however, involve the following problems. Since the diallyl phthalate-based polymer has no photo-reactivity, a photopolymerization initiator should be used in said composition systems in a larger amount than in composition systems composed of a radical-polymerizable monomer and an oligomer in order to attain a practical curing rate. In addition, when a large amount of the aforesaid diallyl phthalate-based polymer is added for controlling the polymerization shrinkage and improving the adhesive properties to a substrate, the viscosity is extremely increased, so that the printability involving leveling properties, appearance and the like is deteriorated.

When the composition system disclosed is used as colored printing ink, its curing rate tends to decrease as compared with an uncolored composition, because of remarkable light absorption by a dye or pigment for the coloring. Therefore, a larger amount of a photopolymerization initiator was necessary in order to attain a practical curing rate.

Moreover, when the amount of the photopolymerization initiator is increased in order to improve the curability, the surface curability is improved but the curability in depth was not sufficient

owing to remarkable light absorption in the surface layer, resulting in that the adhesive properties of the resulting coating film to a substrate is deteriorated.

Thus, it has been difficult to impart all of
5 three conflicting characteristics, i.e., a low viscosity, low shrink properties and a rapid-curability to a solvent-free radiation curable resin composition in all the fields where the resin composition is applied. For solving this problem, a method of foaming
10 the resin composition during curing in order to prevent cure shrinkage, and a method of adding solid fine particles as disclosed in JP-A-7-228644, etc. have been proposed. These methods, however, are disadvantageous in that when the resin composition obtained by either
15 of the methods is used as a coating material, the resulting cured coating film has an unsatisfactory appearance.

The reactive microgels disclosed in Japanese Patent No. 2703125 and JP-B-6-25210 are crosslinked
20 fine particles with a small particle size and reactivity and hence have no undesirable influence on the appearance of coating, so that they might be capable of solving the above problems. However, although these microgels are suitable for use in a
25 resist composition for lithographic plate, they cannot achieve the attainment of a low viscosity intended according to the present invention, for the following reason. The crosslinking density of particles of the

microgel are so low that a solvent-free coating material cannot be obtained by mixing fine particles of the microgel with another radical-polymerizable monomer because the fine particle is swelled by the radical polymerizable monomer during the mixing. The low viscosity was not obtained with those microgels.

Thus, conventional radiation curable resins cannot have all of the three characteristics, a low viscosity, low shrink properties and a rapid-curability. Also in the production of a heat-cured coating film or a heat-cured molded article, there was a problem with attaining both a low viscosity and low shrink properties.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a resin composition having all of the above-mentioned various properties at the same time and a crosslinked-fine-particle dispersion type curable resin composition using the aforesaid resin composition, by dispersing specific crosslinked fine particles in an radiation curable resin or a thermosetting resin composition.

The present inventors earnestly investigated in order to solve the above problems, and consequently found that all of the three characteristics, a low viscosity, low shrink properties and a rapid-curability can be attained at the same time by dispersing

crosslinked fine particles (A) obtained by polymerizing
a compound (a_1) having one or two radical-polymerizable
ethylenic unsaturated groups in the molecule and a
compound (a_2) having three or more (meth)acryloyl groups
5 in the molecule, in a compound (B) having at least one
(meth)acryloyl group in the molecule.

That is, the present invention is a curable
resin composition substantially free of water and
solvents which is characterized by comprising
10 crosslinked fine particles (A) with an
average primary-particle diameter in a range of 10 to
1,000 nm obtained by polymerizing a compound (a_1) having
one or two radical-polymerizable ethylenic unsaturated
groups in the molecule and a compound (a_2) having three
15 or more (meth)acryloyl groups in the molecule, and
a compound (B) having at least one
(meth)acryloyl group in the molecule.

The use of the crosslinked fine particles of
the present invention enabled the same extent of
20 shrinkage reduction with less viscosity increase as
compared with the case where the conventional polymer
or oligomer was incorporated. Moreover, the curing
rate can be overwhelmingly increased. Therefore, a
curable resin composition can be obtained which
25 satisfies all of three characteristics, i.e., a low
viscosity, low shrinkage properties and a rapidly-
curability unlike conventional radiation curable resin
compositions. Accordingly, said crosslinked fine

particles are useful in various fields such as the fields of casting resins, coating materials, adhesives, inks, stereo lithography, photoresists, etc.

PREFERRED EMBODIMENT OF THE INVENTION

5 The components of the resin composition and crosslinked-fine-particle dispersion type resin composition of the present invention are explained below in detail.

 In the present specification, the term
10 “(meth)acrylic acid” means “acrylic acid and/or methacrylic acid”, and the term “(meth)acryloyl group” means “acryloyl group and/or methacryloyl group”.

 The crosslinked fine particles (A) which
15 constitute the present invention are fine particles obtained by polymerizing a compound (a_1) having one or two radical-polymerizable ethylenic unsaturated groups in the molecule and a compound (a_2) having three or more (meth)acryloyl groups in the molecule. In the present
20 specification, the crosslinked fine particles (A) refer to dried ones which are free of water and organic solvents.

 The structure of the crosslinked fine
 particles (A) used in the present invention is not
25 particularly limited and may be any of a single-layer structure, core/shell structure, laminated structure, etc.

The crosslinked fine particles (A) used in the present invention has the following characteristics not attained before: they do not only cause a slight viscosity increase when added to a dispersion medium
5 component (B), but they decrease the polymerization shrinkage of the resin composition.

The component (a_1) used for obtaining the crosslinked fine particles (A) is a compound (a_1) having one or two radical-polymerizable ethylenic unsaturated
10 groups in the molecule, and may be properly chosen in view of the purpose of use, required properties, etc. of the resin composition of the present invention.

Specific examples of the component (a_1) include aromatic vinyl monomers such as styrene, α -
15 methylstyrene, α -chlorostyrene, vinyltoluene, divinylbenzene, etc.; vinyl ester monomers such as vinyl acetate, vinyl butyrate, N-vinylformamide, N-vinylacetamide, N-vinyl-2-pyrrolidone, N-vinylcaprolactam, divinyl adipate, etc.; vinyl ethers
20 such as ethyl vinyl ether, phenyl vinyl ether, etc.; acrylamides such as acrylamide, N-methylolacrylamide, N-methoxymethyl acrylamide, N-butoxymethyl acrylamide, N-t-butyl acrylamide, acryloylmorpholine, methylenebisacrylamide, etc.; (meth)acrylic acid; and
25 (meth)acrylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, hexyl

(meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl
(meth)acrylate, stearyl (meth)acrylate,
tetrahydrofurfuryl (meth)acrylate, 2-hydroxyethyl
(meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-
5 hydroxybutyl (meth)acrylate, glycidyl (meth)acrylate,
dimethylaminomethyl (meth)acrylate, diethylaminomethyl
(meth)acrylate, benzyl (meth)acrylate, cyclohexyl
(meth)acrylate, phenoxyethyl (meth)acrylate,
tricyclodecane (meth)acrylate, allyl (meth)acrylate, 2-
10 ethoxyethyl (meth)acrylate, isobornyl (meth)acrylate,
phenyl (meth)acrylate, ethylene glycol
di(meth)acrylate, polyethylene glycol di(meth)acrylate,
1,3-butylene glycol di(meth)acrylate, 1,4-butanediol
di(meth)acrylate, 1,6-hexanediol di(meth)acrylate,
15 neopentyl glycol di(meth)acrylate, neopentyl glycol
hydroxypivalate di(meth)acrylic acid ester,
polypropylene glycol di(meth)acrylate, bisphenol A
polyoxyethylene di(meth)acrylate, hydrogenated
bisphenol A polyoxyethylene di(meth)acrylate,
20 hydrogenated bisphenol A di(meth)acrylate,
cyclohexanedimethanol di(meth)acrylate, cyclohexanediol
di(meth)acrylate, tricyclodecanedimethanol
di(meth)acrylate, polytetramethylene glycol
di(meth)acrylate, etc. Among these, preferred are
25 (meth)acrylic acid, methyl (meth)acrylate, ethyl
(meth)acrylate, propyl (meth)acrylate, n-butyl
(meth)acrylate, i-butyl (meth)acrylate, t-butyl
(meth)acrylate, ethylene glycol di(meth)acrylate, 1,3-

butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, etc.

The above-exemplified compounds may be used
5 either singly or in combination.

Next, the component (a_2) used for obtaining the crosslinked fine particles (A) is a compound having three or more (meth)acryloyl groups in the molecule. This compound (a_2) having three or more (meth)acryloyl
10 groups has a high reactivity and an excellent crosslinking effect and hence is a crosslinking agent component necessary for crosslinking the above-mentioned component (a_1) at a high density.

Furthermore, the synthesis of the crosslinked fine
15 particles by using the crosslinking agent (a_2) with three or more (meth)acryloyl groups enables to leave a large number of radical-polymerizable ethylenic unsaturated groups derived from the crosslinking agent, on the surfaces and/or in their inner parts of the
20 crosslinked fine particles.

In the present invention, when only a compound having two (meth)acryloyl groups is used as a crosslinking agent in place of the component (a_2), crosslinked fine particles having a low crosslinking
25 density tend to be obtained. Therefore, when these fine particles are dispersed in the compound (B) having at least one (meth)acryloyl group in the molecule, the component (B) infiltrates into the fine particles, so

that the viscosity of the resulting resin composition tends to be extremely increased. In this case, the number of radical-polymerizable ethylenic unsaturated group remaining in the crosslinked fine particles tends to be very small, so that it tends to be impossible to increase the curing rate of the curable composition containing the crosslinked fine particles.

Specific examples of the component (a₂) include (meth)acrylic acid esters such as trimethylolpropane tri(meth)acrylic acid ester, ethoxylated trimethylolpropane tri(meth)acrylic acid ester, propoxylated trimethylolpropane tri(meth)acrylic acid ester, glycerol tri(meth)acrylic acid ester, ethoxylated glycerol tri(meth)acrylic acid ester, tris(acryloxyethyl) isocyanurate, ditrimethylolpropane tetra(meth)acrylic acid ester, pentaerythritol tri(meth)acrylic acid ester, pentaerythritol tetra(meth)acrylic acid ester, dipentaerythritol penta(meth)acrylic acid ester, dipentaerythritol hexa(meth)acrylic acid ester, etc.; urethane poly(meth)acrylates obtained by adding a (meth)acrylate having a hydroxyl group [e.g. 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate and a caprolactone adduct thereof] to a trimer or higher-order oligomer of a diisocyanate compound [e.g. hexamethylene diisocyanate, isophorone diisocyanate, tolylene diisocyanate, xylylene diisocyanate, diphenylmethane diisocyanate and

hydrogenated diphenylmethane diisocyanate]; and epoxy poly(meth)acrylates obtained by adding (meth)acrylic acid to a polyepoxy compound having three or more epoxy groups in the molecule, such as a trifunctional or
5 higher-order polyfunctional phenolic novolak type epoxy resin, a trifunctional or higher-order polyfunctional cresol novolak type epoxy resin, pentaerythritol polyglycidyl ether, trimethylolpropane triglycidyl ether, triglycidyltris(2-hydroxyethyl) isocyanurate
10 or the like. Among these compounds, when trimethylolpropane tri(meth)acrylic acid ester, ditrimethylolpropane tetra(meth)acrylic acid ester, pentaerythritol tri(meth)acrylic acid ester, pentaerythritol tetra(meth)acrylic acid ester,
15 dipentaerythritol penta(meth)acrylic acid ester, dipentaerythritol hexa(meth)acrylic acid ester or the like are used, double bonds derived from the compound (a_2) tend to be well left on polymerizing the compounds (a_1) and (a_2), which is desirable.

20 The above-exemplified compounds may be used either singly or in combination.

 In the present invention, the proportions of the compounds constituting the crosslinked fine particles (A), i.e., the compound (a_1) having one or two
25 radical-polymerizable ethylenic unsaturated groups in the molecule and the compound (a_2) having three or more (meth)acryloyl groups in the molecule are not particularly limited. The proportion of the component

(a₁) ranges preferably from 55 to 95 wt%, more preferably, 65 to 95 wt%, in the total proportion (100 wt%) of the component (a₁) and the component (a₂). The proportion of the component (a₂) ranges preferably from 5 to 45 wt%, more preferably, 5 to 35 wt%.

When the proportion of the component (a₂) relative to the component (a₁) is less than 5 wt%, the crosslinking density of the crosslinked fine particles becomes low. Therefore, when the resulting fine particles are dispersed in the radical-polymerizable unsaturated compound (B), the component (B) infiltrates into the fine particles, so that the viscosity of the resulting resin composition tends to be extremely increased. When the proportion of the component (a₂) relative to the component (a₁) is more than 45 wt%, gelation tends to take place during the polymerization.

In the present invention, the crosslinked fine particles, component (A), can be obtained by polymerization by a well-known polymerization method. An emulsion polymerization method is especially preferable.

The emulsion polymerization method is not particularly limited. There may be adopted any of, for example, a mixing-in-one-lot polymerization method, monomer dropping method, pre-emulsion method, seed polymerization method, multi-stage (core/shell) polymerization method, etc.

When the above-exemplified emulsion

polymerization method is adopted, the polymerization is preferably carried out with the use of an emulsifying agent in order to produce the crosslinked fine particles industrially.

5 Specific examples of emulsifying agent suitable for obtaining the crosslinked fine particles used in the present invention include nonionic surfactants such as polyethylene glycol nonylphenyl ether, polyethylene glycol dodecylphenyl ether, etc.;
10 anionic surfactants such as sodium lauryl sulfate, sodium laurylbenzenesulfonate, sodium dodecylbenzenesulfonate, sodium dialkylsulfosuccinates, etc.; and reactive surfactants such as polyoxyethylene alkylphenyl ether acrylic acid esters, polyoxyethylene
15 alkylpropenylphenyl ethers, polyoxyethylene alkylpropenylphenyl ether sulfuric acid ester ammonium salts, ammonium salt of α -sulfo- ω -(1-((nonylphenoxy)methyl)-2-(2-propenyloxy)ethoxy)-poly(oxy-1,2-ethanediyl), etc.

20 Among the above-exemplified emulsifying agents, the anionic surfactants superior in emulsifying pability are preferable. Radical-reactive anionic surfactants that can be incorporated into the fine particles are more preferable for improving the
25 durability of a coating film.

 The proportion of the emulsifying agent used is preferably 0.1 to 8 wt% based on the total weight of the component (a₁), the component (a₂) and pure water at

the time of emulsion polymerization. Specifically, the following proportions are preferable: pure water 100 to 300 parts by weight, the total amount of the component (a_1), and the component (a_2) (= polymerizable monomers) 5 50 to 150 parts by weight, and the emulsifying agent 0.45 to 13 parts by weight.

The crosslinked fine particles (A) thus obtained are blended with the compound (B) after being dried by water removal.

10 The component (A) used in the present invention refers to one which is in a dried and pulverized state. A method for drying is not particularly limited and includes a method comprising coagulation, washing, drying and then pulverization, a 15 spray drying method, etc.

For example, when the curable resin composition of the present invention is utilized as an radiation curable resin composition, the spray drying method is preferably adopted because it gives fine 20 particles (A) having a small average particle diameter of aggregated particles, which tend to be easily dispersed when mixed with a resin composition.

The average primary-particle diameter of the cross-linked fine particles (A) used in the present 25 invention ranges from 10 to 1,000 nm. The reason is as follows. When the average primary-particle diameter of the component (A) is less than 10 nm, the viscosity of the resulting resin composition tends to be extremely

increased. When the average primary-particle diameter of the component (A) is more than 1,000 nm, the appearance of a cured coating film of the resulting resin composition tends to be unsatisfactory.

5 The especially preferable range of the average primary-particle diameter is 50 to 800 nm. The average primary-particle diameter ranges more preferably from 50 to 250 nm from the viewpoint of the transparency of a coating film.

10 In the present invention, the percentage of cubical expansion of the crosslinked fine particles (A) in methyl ethyl ketone at 25°C is not particularly limited. The percentage of cubical expansion is preferably 300% or less because when such fine
15 particles are dispersed in the radical-polymerizable unsaturated compound (B), the viscosity of the resulting resin composition tends to be not extremely increased when the component (B) infiltrates into the fine particles. The percentage of cubical expansion is
20 preferably, in particular, 250% or less.

 In order to obtain the crosslinked fine particles (A) having a percentage of cubical expansion in methyl ethyl ketone at 25°C of 300% or less, the proportions of the compounds constituting the
25 crosslinked fine particles (A), i.e., the ethylenic unsaturated compound (a_1) and the compound (a_2) having three or more (meth)acryloyl groups in the molecule are as follows: in the total proportion (100 wt%) of the

component (a_1) and the component (a_2), the proportion of the component (a_1) ranges preferably from 95 to 65 wt%, and the proportion of the component (a_2) ranges from 5 to 35 wt%.

5 In the present invention, the percentage of cubical expansion (%) in methyl ethyl ketone of the crosslinked fine particles (A) is calculated by the following method.

 The primary-particle diameter of crosslinked
10 fine particles obtained by the above-mentioned emulsion polymerization method is measured at 25°C by a dynamic light scattering method, and the average particle diameter of the crosslinked fine particles is taken as R_1 . The dried and pulverized to obtain crosslinked fine
15 particles (A) are re-dispersed in methyl ethyl ketone at 25°C and their average particle diameter is measured by using the same system as above. This average particle diameter is taken as R_2 .

 A method for dispersing the crosslinked fine
20 particles (A) in methyl ethyl ketone is not particularly limited. The crosslinked fine particles (A) can be dispersed by the use of any dispersing machine such as a homodisper, dissolver, three roll mill, ball mill or the like after being mixed with
25 methyl ethyl ketone. The percentage of cubical expansion (%) in an organic solvent of the crosslinked fine particles is represented by V (%) in the following equation:

$$V = (R_2)^3 / (R_1)^3 \times 100$$

The amount of double bonds remaining in the dried and pulverized crosslinked-fine-particles (A) used in the present invention is preferably 0.01 mmol/g or more. When the amount of the remaining double bonds is less than 0.01 mmol/g, the curability of the resulting curable composition containing the crosslinked fine particles (A) dispersed therein tends to be not improved, which is not desirable. Although a method for determining the amount of the remaining double bonds is not particularly limited, a value determined by the following determination method is defined as the amount of the remaining double bonds in the present invention.

One gram of the crosslinked fine particles (A) obtained are accurately measured (the accurately measured amount is taken as x g), and then the crosslinked fine particles accurately measured, 20 g of water and 4 g of tetrahydrofuran (THF) are placed in a 200-ml flask and stirred for 30 minutes. To the resulting mixture are added 10 ml of a 0.1N KBrO₃ aqueous solution and 5 ml of 6N HCl, immediately after which the flask was closed with a plug, followed by stirring in the dark for 5 minutes. Bromine is thus produced and added to double bonds remaining in the crosslinked fine particles. After the flask was allowed to stand in a dark room for 30 minutes, 5 ml of

a 15 wt% KI aqueous solution is added into the flask while cooling the flask with ice water, and the resulting mixture is stirred for 5 minutes. By this stirring, non-added bromine is replaced with iodine.

5 The iodine produced is titrated with a 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution. The titration end point is a point at which the color of the dark-brown liquid changes to colorless or yellow. The amount of the remaining double bonds is determined from the titer according to

10 the following equation:

$$\begin{aligned} \text{Amount of remaining double bonds (mmol/g)} = \\ & 1/2 \times [(\text{titer for blank}) - (\text{titer for sample})] \times \\ & 0.1 \times f \times (1/x) \end{aligned}$$

wherein the titer for blank is the titer (ml) of the

15 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution measured in the case of not using the sample (the fine particles) in the above determination method; the titer for sample is the titer (ml) of the 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution measured in the case of using the sample (the fine particles) in the

20 above determination method; f is a factor for 0.1N $\text{Na}_2\text{S}_2\text{O}_3$; and x is the amount (g) of the sample (the fine particles) accurately measured.

The glass transition temperature (T_g) of the dried and pulverized crosslinked-fine-particles (A)

25 used in the present invention is preferably 100°C or higher. When the glass transition temperature (T_g) is

lower than 100°C, the curability of the resulting curable composition containing the crosslinked fine particles (A) dispersed therein tends to be not improved, which is not desirable. A method for
5 measuring the Tg is not particularly limited. In the present invention, the dried and pulverized crosslinked-fine-particles (A) are placed directly on a glass stage, and the Tg is defined as a thermal and mechanical value determined from a change of the
10 thermal expansion coefficient by using the TMA method.

The resin composition of the present invention is obtained by blending by dispersion the crosslinked fine particles (A) with the component (B). A method for dispersing the component (A) in the
15 component (B) to blend them is not particularly limited. The component (A) can be dispersed in component (B) by the use of any dispersing machine such as a homodisper, dissolver, triple-roll mill, ball mill or the like after being mixed with the component (B).

20 In the present invention, the compound (B) having at least one (meth)acryloyl group in the molecule is used as a dispersion medium for the component (A).

As specific examples of the component (B),
25 the (meth)acrylic acid esters mentioned above as specific examples of the component (a₁), and the component (a₂) can be used. In addition to them, there can be mentioned, for example, polyester

poly(meth)acrylates obtained by the reaction of a polybasic acid [e.g. phthalic acid and adipic acid], a polyhydric alcohol [e.g. ethylene glycol, hexanediol, poly(ethylene glycol)s, poly(tetramethylene glycol)s] and (meth)acrylic acid or its derivative; epoxy poly(meth)acrylates obtained by reacting a glycidyl ether compound [e.g. bisphenol A diglycidyl ether and ethylene glycol diglycidyl ether] with a (meth)acrylic acid or its derivative; and urethane poly(meth)acrylates obtained by reacting an isocyanate compound [e.g. hexamethylene diisocyanate, isophorone diisocyanate, tolylene diisocyanate, xylylene diisocyanate, diphenylmethane diisocyanate, and hydrogenated diphenylmethane diisocyanate] with a (meth)acrylate having a hydroxyl group [e.g. 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate].

These may be used either singly or in combination.

The proportions of the crosslinked fine particles (A) and the compound (B) are as follows: in the total proportion (100 wt%) of the component (A) and the component (B), the proportion of the component (A) ranges from 5 to 50 wt%, and the proportion of the component (B) ranges from 50 to 95 wt%.

When the proportion of the component (A) is more than 50 wt%, the resulting resin composition has a high viscosity, so that its coatability tends to be

poor. When the proportion of the component (A) is less than 5 wt%, the curability and low shrink properties intended according to the present invention tend to be not sufficiently exhibited.

5 It is preferable to incorporate radical polymerization initiators (C) such as photopolymerization initiators (C₁), thermal polymerization initiators (C₂) and the like properly into the curable resin composition of the present invention.

10 Specific examples of the photopolymerization initiators (C₁) include benzophenone, 4,4-bis(diethylamino)benzophenone, t-butylanthraquinone, 2-ethylanthraquinone, and thioxanthenes (e.g. 2,4-diethylthioxanthone, isopropylthioxanthone and 2,4-dichlorothioxanthone); acetophenones such as 15 diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-2-morpholino(4-thiomethylphenyl)propan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone, etc.; 20 benzoin ethers such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, etc.; acylphosphine oxides such as 2,4,6-trimethylbenzoyl-diphenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, 25 bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, etc.; methylbenzoyl formate; 1,7-bisacrydinylheptane;

9-phenylacridine; etc.

These photopolymerization initiators (C_1) may be used singly or in combination and are incorporated into the present resin composition comprising the component (A) and the component (B), in a proportion of preferably 0.01 to 20 parts by weight, in particular, 0.1 to 10 parts by weight, per 100 parts by weight of the resin composition.

In addition, if necessary, well-known photosensitizers such as methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, amyl 4-dimethylamino-benzoate, 4-dimethylaminoacetophenone, etc. may be incorporated into the curable resin composition of the present invention.

Specific examples of the thermal polymerization initiators (C_2) include organic peroxides such as methyl ethyl ketone peroxide, benzoyl peroxide, dicumyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide, t-butyl peroxyoctoate, t-butyl peroxybenzoate, lauroyl peroxide, etc.; azo compounds such as azobisisobutyronitrile, etc.; and redox polymerization initiators obtained by combining amines (e.g. N,N-dimethylaniline and N,N-dimethyl-p-toluidine) with any of the above-mentioned peroxides. The 10-hours half-life temperature of these thermal polymerization initiators (C_2) is preferably 100°C or lower. If a thermal polymerization initiator having a

10-hours half-life temperature of higher than 100°C is used, the curing rate tends not to be increased.

If necessary, metal soaps such as cobalt naphthenate, manganese naphthenate, nickel octylate,
5 etc. may also be used.

These thermal polymerization initiators (C_2) may be used either singly or in combination and are incorporated into the resin composition comprising the component (A) and the component (B), in a proportion of
10 preferably 0.001 to 10 parts by weight, in particular, 0.01 to 5 parts by weight, per 100 parts by weight of the resin composition.

In addition, well-known additives such as mold release agents, lubricants, plasticizers,
15 antioxidants, ultraviolet absorbers, flame retardants, flame-retarding assistants, polymerization inhibitors, fillers, organic solvents usable in the present invention, pigments, dyes, silane coupling agents, etc. may be properly used depending on their purpose, in the
20 resin composition and crosslinked-fine-particle dispersion type curable resin composition of the present invention.

The curable resin composition of the present invention is useful as a composition substantially free
25 of water and solvents. The viscosity of said composition is preferably 10 Pa·s or less at 25°C, more preferably 5 Pa·s or less at 25°C, from the viewpoint of work-efficiency. A curable resin composition having

a viscosity of more than 10 Pa·s at 25°C requires heating in some cases at the time of coating or printing in order to reduce the viscosity and, thus, tends to result in the deterioration of the productivity. Moreover, even if the application or printing with such composition is possible the appearance of the resulting coating or print tends to be unsatisfactory, which is not desirable.

The curable resin composition of the present invention can be used in any of the fields of molded articles, adhesives, coating materials, inks, resins for stereo lithography, photoresists, etc. A method for curing said resin composition is not particularly limited, and the resin composition can be cured by various curing methods well known and conventionally used in the fields mentioned above.

In particular, said resin composition causes only a slight viscosity increase when added to a dispersion medium, is excellent in curability and can have low shrink properties. Therefore, said resin composition can exhibit its performance characteristics to the utmost when used as an radiation curable resin which can be used, for example, for film coatings and wood coatings and in printing inks.

The present invention is concretely illustrated below with examples and comparative examples.

Example 1

[Preparation of a starting pre-emulsion]

A pre-emulsion was obtained by mixing 55 parts by weight of methyl methacrylate, 30 parts by weight of n-butyl methacrylate, 15 parts by weight of PETA (a mixture consisting of 60% of pentaerythritol triacrylate and 40% of pentaerythritol tetraacrylate), 0.3 part by weight of a peroxide initiator (Perbutyl H, a trade name, mfd. by Nippon Oils and Fats Co., Ltd.), 3 parts by weight of sodium dodecylbenzene- sulfonate and 55 parts by weight of pure water, and stirring the resulting mixture continuously.

[Preparation of crosslinked fine particles]

In a 2-liter four-necked flask were placed 145 parts by weight of pure water, 0.3 part by weight of Rongalite, 0.01 part by weight of ethylenediamine-N,N,N',N'-tetraacetic acid disodium salt and 0.0025 part by weight of ferrous sulfate heptahydrate, and they were stirred at 150 rpm with an anchor-shaped stirring rod.

After the air in the system was replaced with nitrogen gas introduced into the system, the temperature was begun to be raised. When the internal temperature reached 60°C, dropwise addition of the pre-emulsion was started and 40 parts by weight of the pre-emulsion was added dropwise in 30 minutes, followed by continuous stirring at an internal temperature of 60°C

for 30 minutes. Then, the whole of 120 parts by weight of the residual starting pre-emulsion was added dropwise in 2 hours. The resulting mixture was continuously stirred for 2 hours while maintaining the internal temperature at 60°C, and was then cooled to obtain a milk-white emulsion. A portion of the obtained emulsion was sampled and its average primary-particle diameter R_1 at 25°C was measured with a dynamic light-scattering photometer DLS-600 manufactured by Otsuka Electronics Co., Ltd. The result obtained is shown in Table 1.

The obtained emulsion was subjected to spray drying with a spray dryer Model L-8 manufactured by Ohkawara Kakohki Co., Ltd., to obtain crosslinked fine particles (P1).

The spray drying conditions were as follows: chamber inlet temperature of 120°C, chamber outlet temperature of 60°C, and the number of revolution of an atomizer of 25,000 rpm. The thus obtained powder contained no blocking substance and had a high fluidity.

[Preparation of a dispersion of the fine particles in methyl ethyl ketone]

A milk-white resin composition was obtained by mixing 20 parts by weight of the crosslinked fine particles (P1) obtained and 80 parts by weight of methyl ethyl ketone, and stirring the resulting mixture

in a homodisper for 5 minutes at a number of revolution of 2,000 rpm. A portion of the obtained milk-white resin composition was sampled and its average primary-particle diameter R_2 at 25°C was measured with a dynamic
5 light-scattering photometer DLS-600 manufactured by Otsuka Electronics Co., Ltd. The result obtained is shown in Table 1.

[Evaluation of the percentage of cubical expansion of the crosslinked fine particles in the organic solvent]
10 The percentage of cubical expansion of the crosslinked fine particles in the organic solvent was calculated from the average primary-particle diameter R_1 of the emulsion in water after the emulsion polymerization and the average primary-particle
15 diameter R_2 of the fine particles in methyl ethyl ketone, and is shown in Table 1.

[Evaluation of the amount of double bonds remaining in the crosslinked fine particles]

One gram of the crosslinked fine particles
20 (P1) obtained were accurately measured (the accurately measured amount is taken as x g), and then the crosslinked fine particles accurately measured, 20 g of water and 4 g of tetrahydrofuran (THF) were placed in a 200-ml flask and stirred for 30 minutes. To the
25 resulting mixture were added 10 ml of a 0.1N KBrO₃ aqueous solution and 5 ml of 6N HCl, immediately after

which the flask was closed with a plug, followed by stirring in the dark for 5 minutes (bromine is thus produced and added to double bonds remaining in the crosslinked fine particles). After the flask was
5 allowed to stand in a dark room for 30 minutes, 5 ml of a 15 wt% KI aqueous solution was placed in the flask while cooling the flask with ice water, and the resulting mixture was stirred for 5 minutes (bromine not added to double bonds is replaced with iodine in
10 this way). The iodine produced was titrated with a 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution. The titration end point was a point at which the color of the dark-brown liquid had changed to colorless or yellow. Table 1 shows the result of determining the amount of the remaining
15 double bonds from the titer according to the following equation:

$$\begin{aligned} \text{Amount of remaining double bonds (mmol/g)} = \\ \frac{1}{2} \times [(\text{titer for blank}) - (\text{titer for sample})] \times \\ 0.1 \times f \times (1/x) \end{aligned}$$

20 wherein the titer for blank is the titer (ml) of the 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution measured in the case of not using the sample (the fine particles) in the above determination method; the titer for sample is the titer (ml) of the 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution measured in the
25 case of using the sample (the fine particles) in the above determination method; f is a factor for 0.1N

$\text{Na}_2\text{S}_2\text{O}_3$; and x is the amount (g) of the sample (the fine particles) accurately measured.

[Evaluation of the glass transition temperature of the crosslinked fine particles]

5 The crosslinked fine particles (P1) obtained were placed directly on a glass stage and subjected to TMA measurement in a temperature range of 20°C to 250°C at a heating rate of 10°C/min by using a quartz probe. A tempera-
10 ture at which the expansion coefficient had changed was determined from a thermal expansion curve measured by the TMA method and is shown as Tg in Table 1.

[Preparation of an radiation curable resin composition]

 Thirty parts by weight of the crosslinked
15 fine particles (P1) obtained, 20 parts by weight of dipentaerythritol hexaacrylate, 50 parts by weight of tripropylene glycol diacrylate and 5 parts by weight of 1-hydroxycyclohexyl phenyl ketone as a
 photopolymerization initiator were mixed and then
20 stirred for 5 minutes in a homodisper at a number of revolution of 4,000 rpm to obtain a milk-white radiation curable resin composition. The evaluation results of film performance for the resin composition are described below.

25 [Evaluation of the radiation curable resin composition]

For the radiation curable resin composition obtained, the E-type viscosity at 25°C and the polymerization shrinkage determined from the difference between the specific gravities of the liquid composition and a cured product thereof are shown in Table 2.

Curability:

The resin composition was applied on the primer-coated surface of a PET film A-4100 manufactured by Toyobo Co., Ltd., with a bar coater #3, and was irradiated with ultraviolet rays from a high-pressure mercury lamp of 120 w/cm at a lamp height of 10 cm and a conveyor speed of 50 m/min. Table 2 shows a number of irradiation operations at which the cured film surface became tack-free in a dry to the touch test.

A criterion for evaluation by the dry to the touch test is as follows:

- Good: The cured film surface became tack-free after two or less runs of the irradiation.
- 20 Fair: The cured film surface became tack-free after not more than 5 and not less than 3 runs of the irradiation.
- Poor: The cured film surface became tack-free after 6 or more runs of the irradiation.

25 Coatability:

The appearance of the cured film was visually evaluated.

Good: a flat surface having a good appearance.

Fair: the presence of a few stripes formed by the bar coater.

5 Poor: unusable because of remarkable unevenness of the surface.

Adhesive properties:

A cellophane adhesive tape (mfd. by Nichiban Co., Ltd.) was stuck on the cured film obtained in the curability evaluation, and was quickly peeled off, 10 after which the adhered state of the cured film was visually evaluated (a no-cut test). In this case, when the cured film would not be peeled off, notches were made crosswise on the cured film with a cutter knife and the adhered state of the cured film was visually 15 evaluated in the same manner as above (a cross-cut test). A criterion for the evaluation was as follows:

Good: The film was peeled off in neither the no-cut test nor the cross-cut test.

20 Fair: The film was not peeled off in the no-cut test but was peeled off in the cross-cut test.

Poor: The film was peeled off in the no-cut test.

Odor:

The cured film obtained in the curability evaluation was allowed to stand at 20°C and 50% RH for 25 24 hours, and then subjected to an organoleptic test for odor by maintaining the position of nose at a

height of 2 cm above the cured film. The odor was evaluated according to the following criterion:

Good: substantially no odor.

Fair: a slight odor.

5 Poor: a strong odor.

Warpage of the PET film:

The PET film after the coating and the curing obtained in the curability evaluation was allowed to stand at 20°C and 50% RH for 24 hours, and then cut to a
10 size of A4. Then, the sample piece thus obtained was allowed to stand on a plane with the cured film side upward, after which the degree of lifting from the plane was measured for the four corners of the sample piece and the average of the measured values was
15 calculated. The warpage was evaluated according to the following criterion:

Good: The average degree of lifting was less than 3 mm.

Fair: The average degree of lifting was 3 mm to
20 5 mm.

Poor: The average degree of lifting was more than 5 mm.

Examples 2 to 4 and Comparative Example 1

Crosslinked fine particles (P2 to P6) having
25 the compositions shown in Table 1 were synthesized by the same process as in Example 1. The crosslinked fine

particles of each kind were dispersed in the component (B) to blend them according to the recipe shown in Table 2 as in Example 1, whereby radiation curable resin compositions were obtained. These compositions were evaluated in the same manner as in Example 1.

The evaluation results are shown in Table 2.

Example 5

Blending was conducted in the same manner as in Example 1 except for using benzoyl peroxide as a thermal polymerization initiator in place of the photopolymerization initiator among the components used in the Example 1. The resulting resin composition was applied on a glass substrate with a bar coater #3 and cured in an oven at 120°C for 10 minutes, and the E-type viscosity and the polymerization shrinkage were determined in the same manner as in Example 1. E-type viscosity was 400 mPa·s and the polymerization shrinkage 9.1%. The cured film thus obtained showed the transparency and good appearance.

Comparative Examples 2 to 7

The compositions shown in Table 2 were obtained by blending and subjected to evaluation of viscosity, polymerization shrinkage, curability, coating efficiency, adhesive properties and film warpage in the same manner as in the case of the radiation curable resin composition obtained in Example 1.

Table 1

		P1	P2	P3	P4	P5
Compound (a ₁)	MMA	55	40	60	50	55
	nBMA	30	30			30
	THFMA			30		
	ACMO				30	
	BD					15
Compound (a ₂)	TMPTA		30			
	PETA	15		10	20	
R1 (nm)		180	150	130	90	150
R2 (nm)		230	160	170	110	280
Percentage of cubical expansion (%)		208	121	224	183	650
Amount of double bonds (mmol/g)		0.024	0.018	0.016	0.032	0.006
Tg (°C)		130	150	125	160	95

The abbreviations in Table 1 are as follows:

MMA: methyl methacrylate, nBMA: n-butyl methacrylate,

THFMA: tetrahydrofurfuryl methacrylate, ACMO:

acryloylmorpholine, BD: 1,3-butylene glycol

5 dimethacrylate, TMPTA: trimethylolpropane triacrylate,

PETA: a mixture consisting of 60% of pentaerythritol

triacrylate and 40% of pentaerythritol tetraacrylate.

- *1) P6: a linear polymer (weight average molecular weight 20,000) of MMA/nBMA = 62 wt%/38 wt%.
- *2) P7: a polystyrene (weight average molecular weight 20,000).
- 5 *3) P8: crosslinked poly(methyl methacrylate) particles MB20X-5 (average particle diameter 5 μ m) manufactured by Sekisui Plastics Co., Ltd.
- *4) Evaluation was impossible because the compound (B) infiltrated into fine particles (P6) in the
- 10 dispersing operation of the fine particles (P6) in the compound (B), so that the whole resin gelled.

The abbreviations in Table 2 are as follows:

- DPHA: dipentaerythritol hexaacrylate,
- PETA: a mixture consisting of 60% of pentaerythritol
- 15 triacrylate and 40% of pentaerythritol tetraacrylate,
- TPGDA: tripropylene glycol diacrylate,
- HCPK: 1-hydroxycyclohexyl phenyl ketone.

[Preparation of an radiation curable resin composition

20 - 2]

Example 6

Thirty parts by weight of the crosslinked fine particles (P1) obtained, 50 parts by weight of tripropylene glycol diacrylate, 20 parts by weight of

25 urethane acrylate UK-6091 manufactured by Mitsubishi Rayon Co., Ltd. and 3 parts by weight of 1-hydroxycyclohexyl phenyl ketone as a

photopolymerization initiator were mixed and then stirred for 5 minutes in a homodisper at a number of revolution of 4,000 rpm to obtain a milk-white radiation curable resin composition. The evaluation results of the wood coating performance for the resin composition are described below.

[Evaluation of the radiation curable resin composition
- 2]

Table 3 shows the E-type viscosity at 25°C of the radiation curable resin composition obtained in Example 6.

The radiation curable composition obtained was applied on a plywood with a bar coater #60 and irradiated with ultraviolet rays from a high-pressure mercury lamp of 80 W/cm at a lamp height of 15 cm and a conveyor speed of 10 m/min until the cured film surface became tack-free in a dry to the touch test. The cured film thus obtained was subjected to various performance tests. The results obtained are shown in Table 3.

[Performance test methods]

Curability:

A number of ultraviolet irradiation operations required for the cured film surface to become tack-free was measured by touch with a finger, and the curability was evaluated according to the following criterion:

Good: two or less times.

Fair: not more than 5 and not less than 3 times.

Poor: six or more times.

Coating efficiency:

- 5 The appearance of the cured film was visually evaluated.

Good: a flat surface having a good appearance.

Fair: the presence of a few stripes formed by the bar coater.

- 10 Poor: unusable because of remarkable unevenness of the surface.

Polymerization shrinkage:

- The polymerization shrinkage was determined from the specific gravities of the liquid composition and the cured film, and was evaluated according to the following criterion:
- 15

Good: less than 8%.

Fair: not more than 10% and not less than 8%.

Poor: more than 10%.

- 20 Crack resistance:

 A cycle test consisting of standing at 80°C for 2 hours and standing at -20°C for 2 hours per cycle was repeated, and the crack resistance was evaluated in terms of a number of cycles that cause a crack in the coating film.

25

Good: 50 or more cycles.

Fair: 10 to 49 cycles.

Poor: less than 10 cycles.

Examples 7 to 9 and Comparative Example 8

- 5 Crosslinked fine particles (P2 to P5) having
the compositions shown in Table 1 were synthesized by
the same process as in Example 1. The crosslinked fine
particles of each kind were dispersed in the component
(B) to blend them according to the recipe shown in
10 Table 3, as in Example 1, whereby radiation curable
compositions were obtained. Cured films of these
compositions were evaluated in the same manner as in
Example 1.

The evaluation results are shown in Table 3.

- 15 Comparative Examples 9 to 12

The compositions shown in Table 3 were
obtained by blending and subjected to evaluation of
viscosity, curability, coating efficiency,
polymerization shrinkage and crack resistance in the
20 same manner as the evaluation of the radiation curable
resin composition obtained in Example 1.

The evaluation results are shown in Table 3.

Table 3

			Example					Comparative Example				
			6	7	8	9	8	9	10	11	12	
Composition	Fine particles (A)	P1	30									
		P2		40								
		P3			20							
		P4				10						
		P5					30					
		P6						30				
		P8							30			
		Com-pound (B)	UK-6091	20	17	23	26	20	20	20	29	
UK-1102											50	
TPGDA	50		43	57	64	50	50	50	71		50	
Evaluation results	Photo-polymerization initiator HCPK		3	3	3	3	3	3	3	3	3	
		E-type viscosity (mPa·S)	500	600	400	300	- ¹⁵⁾	20000	500	300	400	
		Curability	Good	Good	Good	Good	- ¹⁵⁾	Fair	Poor	Fair	Poor	
		Coating efficiency	Good	Good	Good	Good	- ¹⁵⁾	Poor	Fair	Good	Good	
		Polymerization shrinkage	Good	Good	Good	Good	- ¹⁵⁾	Good	Good	Fair	Fair	
	Crack resistance	Good	Good	Good	Good	- ¹⁵⁾	Good	Fair	Poor	Poor		

*5): Evaluation was impossible because the compound (B) infiltrated into fine particles (P5) in the dispersing operation of the fine particles (P5) in the compound (B), so that the whole resin was gelatinized.

The abbreviations in Table 3 are as follows:

UK-6091: urethane acrylate manufactured by Mitsubishi Rayon Co., Ltd.,

UK-1102: an unsaturated polyester manufactured by Mitsubishi Rayon Co., Ltd.,

TPGDA: tripropylene glycol diacrylate,

HCPK: 1-hydroxycyclohexyl phenyl ketone.

[Preparation of a radiation curable composition - 3]

Example 10

Thirty parts by weight of the crosslinked fine particles (P1) obtained, 50 parts by weight of ditrimethylolpropane tetraacrylate, 20 parts by weight of neopentyl glycol hydroxypivalate diacrylate, 20 parts by weight of Rionol Red F2B (mfd. by TOYO INK MFG. CO., LTD) as a pigment and 3 parts by weight of Irgacure 907 (mfd. by Ciba Speciality Chemicals Ltd.) as a photopolymerization initiator were mixed and then subjected to dispersion with a triple roll mill to obtain a radiation curable composition. The results of evaluation of this composition as printing ink are described below.

[Evaluation of the radiation curable composition - 3]

Table 4 shows the result of measuring the E-type viscosity at 25°C of the radiation curable composition obtained in Example 10.

5 Using the radiation curable composition obtained, printing was conducted on coated paper "NK Kata-Art" (mfd. by Nippon Kakoh Seishi Co., Ltd.) with a screen printer so that the thickness of the composition would be 15 μ m. Then, the printed-paper
10 placed on a conveyor was passed under a metal halide lamp having an intensity of 120 W/cm, at a lamp height of 10 cm. In dry to the touch evaluation, a maximum line speed at which the cured film surface became tack-free was evaluated according to the following
15 criterion.

Curability:

Table 4 shows a maximum line speed at which the radiation curable composition became tack-free owing to the irradiation of one passing when the line
20 speed was increased by increments of 10 m/min.

When a composition was curable at a line speed of 50 m/min or more, the composition was rated eligible. The cured film thus obtained was subjected to performance tests with regard to adhesive properties
25 and appearance of print. The results obtained are shown in Table 4.

Adhesive properties:

A cellophane adhesive tape (mfd. by Nichiban Co., Ltd.) was stuck on the printing and coating film which had been cured, after which the tape was quickly
5 peeled off, and the adhered state of the cured film was visually evaluated (a no-cut test). In this case, when the coating film was not peeled off, notches were made crosswise on the cured film with a cutter knife and the adhered state of the cured film was visually evaluated
10 in the same manner as above (a cross-cut test). The evaluation was carried out according to the following criterion and the result obtained is shown in Table 4:

Good: The film was peeled off in neither the no-cut test nor the cross-cut test.

15 Fair: The film was not peeled off in the no-cut test but was peeled off in the cross-cut test.

Poor: The film was peeled off in the no-cut test.

Appearance of print:

The appearance of the printing was visually
20 evaluated according to the following criterion. The result obtained is shown in Table 2.

Excellent: The appearance of print was so good that it was smooth and had a high gloss.

Good: The appearance of print was smooth but the
25 print surface was matte.

Fair: Curing in depth was not sufficient, resulting

in formation of a few wrinkles on the print surface.

Poor: Print was not cured in depth, resulting in formation of a large number of wrinkles on the print surface.

Warpage of the printed paper:

The printed paper after the curing was allowed to stand at 20°C and 50% RH for 24 hours, and then cut to a size of A4. Then, the sample piece thus obtained was allowed to stand on a plane with the cured film side upward, after which the degree of lifting from the plane was measured for the four corners of the sample piece and the average of the measured values was calculated. The warpage was evaluated according to the following criterion:

Good: The average degree of lifting was less than 3 mm.

Fair: The average degree of lifting was 3 mm to 5 mm.

Poor: The average degree of lifting was more than 5 mm.

Examples 11 to 13 and Comparative Example 13

Crosslinked fine particles (P2 to P5) having the compositions shown in Table 1 were synthesized by the same process as in Example 1. The crosslinked fine particles of each kind were dispersed in the component

(B) to blend them according to the recipe shown in Table 4, as in Example 1, whereby radiation curable compositions were obtained. These compositions were evaluated in the same manner as in Example 1.

5 The evaluation results are shown in Table 4.

Comparative Examples 14 to 18

 The compositions shown in Table 4 were obtained by blending and subjected to evaluation of curability, adhesive properties, appearance of coating,
10 and paper warpage in the same manner as the evaluation of the radiation curable resin composition obtained in Example 1.

 The evaluation results are shown in Table 4.

Table 4

	Example					Comparative Example							
	10	11	12	13	13	13	14	15	16	17	18		
Fine particles (A)													
P1	30												
P2		40											
P3			20										
P4				10									
P5						30							
P9*6)							30	30					
P8									30				
Compound (B)													
DTMPTA	50	43	57	64		50	50	50	50	71	71		
HPNDA	20	17	23	26		20	20	20	20	29	29		
Photo-polymerization initiator	3	3	3	3		3	3	8	3	3	3		8
Pigment	20	20	20	20		20	20	20	20	20	20		20
E-type viscosity (mPa·s)	3000	3500	2000	1000		*7)	6000	6000	3000	800	800		800
Line speed (m/min)	60	60	50	50		*7)	30	50	30	30	50		50
Adhesive properties	Good	Good	Good	Good		*7)	Good	Fair	Poor	Poor	Poor		Poor
Appearance of print	Excellent	Excellent	Excellent	Excellent		*7)	Excellent	Fair	Good	Excellent	Poor		Poor
Paper warpage	Good	Good	Good	Good		*7)	Good	Fair	Fair	Poor	Poor		Poor

- *6) P9: DAP-K (a dially phthalate prepolymer)
manufactured by Daisoh Co., Ltd.
- *7) Further evaluation was impossible because the
compound (B) infiltrated into fine particles (P5)
5 in the dispersing operation of the fine particles
(P5) in the compound (B), so that the whole resin
was gelatinized.